PHOTOCHEMICAL HOLE BURNING MEDIA

Background of the Invention

(1) Field of the Invention

[0001] The present invention relates to optical memories for wavelength multiple-type high density recording, and more particularly the invention relates to optochemical hole burning media.

(2) Related Art Statement

[0002] Optical recording media in which recorded information can be rewritten to another are broadly classified into the heat mode type and the photon mode type according to the operating principles. In the former, different states : (recorded state/erased state) which are optically discernible from each other are reversely changed by utilizing heating and cooling of the medium with irradiation of laser beam. Magneto-optical media, phase transition media, organic media, etc. belong to this type. In the photon mode type, an intrinsic energy of a light determined by its wavelength is directly used to cause reversible optical changes. Photochromic media and optochemical hole burning (PHB) media belong to this type.

[0003] The Persistent Spectral Hole Burning (PSHB) is the phenomenon that when laser beam is irradiated upon a solid in which molecules or ions having optical absorption ability, a hole persistently appears in the spectrum at a wavelength equal to that of the irradiated beam. The hole burning is an effective measure as a high resolution spectroscopy for the solids, and is expected to be applied as a wavelength-multiple type high density optical memory in case that the width (uniform width) of the hole of the hole is smaller than that (non-uniform width) of the absorption spectrum. That is, when the hole burning is effected while the wavelength of the irradiating laser, a plurality of holes independent of one another can be formed in a single spot. If bids of 1 and 0 are made correspondent to the presence and absence of such a hole, the wavelength multiple recording is feasible, so that optical memories at a super high density can be realized. As a material for such an optical memory, materials into which rare earth ions are introduced are known.

[0004] However, the media that are at a practical level or a near practical level are of the heat mode type. In any of the optically recording media of the heat mode

type, recording is effected by using a single-wavelength light, which poses a limit upon the recording capacity.

[0005] On the other hand, the photon mode type is a level of searching fundamental materials. Among the photon mode type optical media, the optochemical hole burning media have the merit that the recording capacity can be greatly increased by overwriting information data at one location at different wavelengths. However, the optochemical hole burning media are still at a level of searching fundamental materials, including the above-mentioned rare earth ion-introduced materials, and materials considered preferable for the optochemical hole burning media are still at a study level. Therefore, materials which can be used for the optochemical hole burning media have been desired to be developed.

Summary of the Invention

[0006] Therefore, it is an object of the present invention to provide optochemical hole burning media which can greatly increase the recording capacity.

[0007] In order to accomplish the above object, the present inventor repeatedly made strenuous studies on materials in which various complexes were dispersed in a SiO_2 matrix, and consequently he discovered materials which can hold holes even at room temperature.

[0008] The photochemical hole burning medium according to the present invention comprises a material in which a rare earth complex and a reducing agent are dispersed in a solid matrix.

[0009] The following are preferred embodiments of the photochemical hole burning medium according to the present invention.

(1) The rare earth complex is at least one complex selected from the group consisting of europium (III) crown ether complexes, europium (III) polyether complexes, and europium (III) cryptand complexes.

[0010]

(2) The reducing agent is an electron-donating composite compound. In this preferred embodiment of the optochemical hole burning medium according to the present invention, the rare earth complex contributing to the formation of the hole and the reducing organic molecules contributing to the stabilization of the hole are held in the form of an electron-donating composite compound in a uniformly dispersed state.

[0011]

(3) The electron-donating composite compound is a silane compound or a disilazane compound.

[0012]

(4) The silane compound is a hexaalkyl disilazane represented by hexamethyl disilane, and the disilazane compound is a hexaalkyl disilazane represented by hexamethyldisilazane.

[0013]

(5) The electron-donating composite compound is an organic tin compound.

[0014]

(6) The organic tin compound is a compound represented by RSnSnR in which R is an alkyl group or an aryl group.

[0015]

(7) The solid matrix is at least one glass-forming compound selected from the group consisting of silica, germanium oxide, boron oxide, phosphorus pentaoxide and tellurium oxide.

[0016]

(8) At least one compound selected from the group consisting of Al_2O_3, Ga_2O_3, In_2O_3, TiO_2, ZrO_2, Nb_2O_5 and Ta_2O_5 is contained in said solid matrix.

[0017] These and other objects, features and advantages of the invention will be appreciated upon reading of the following description of the invention when taken in conjunction with the attached drawings, with the understanding that any modifications, variations and changes could be easily made by the skilled person in the art to which the invention pertains.

[0018] As a further preferable embodiment of the photochemical hole burning medium according to the present invention, the reducing agent has an oxidation/reduction potential of not more than 1 V.

<u>Brief Description of the Drawings</u>

[0019] For a better understanding of the invention, reference is made to the attached drawings, wherein:

Figs. 1(a) to 1(c) are graphs showing excitation spectra of SiO_2-ZrO_2 : $[Eu(15C5)]^{3+}$ before and after irradiation with laser beams.

Figs. 2(a) to 2(c) are graphs showing heat cycle characteristics of SiO_2-

ZrO_2 : $[Eu(15C5)]^{3+}$ in which Figs. 2(a), 2(b) and 2(c) correspond to SiO_2 : ZrO_2 = 7 : 3, SiO_2 : ZrO_2 = 5 : 5, and SiO_2 : ZrO_2 = 3 : 7, respectively.

Figs. 3(a) and 3(b) are graphs showing fluorescent spectra of SiO_2 : $[Eu(15C5)]^{3+}$ before and after laser beam irradiation, respectively.

Figs. 4(a) and 4(b) are graphs showing spectra of the optochemical hole burning media according to an embodiment of the present invention before and after laser beam irradiation, respectively, in which Figs. 4(a) and 4(b) correspond to SiO_2 : $Eu(15C5)^{3+}Me_3SiSiMe_3$ and SiO_2 : $Eu^{3+}Me_3SiSiMe_3$.

Fig. 5 is a graph showing spectra of the optochemical hole burning medium of SiO_2 : $Eu(15C5)^{3+}Me_3SnSnMe_3$ according to another embodiment of the present invention before and after laser beam irradiation.

Figs. 6(a) to 6(c) are graphs showing heat cycle characteristics of optochemical hole burning media a further embodiment according to the present invention in which Fig. 6(a) shows the heat cycle characteristic of SiO_2 : $Eu(15C5)^{3+}Me_3SiSiMe_3$, and Figs. 6(b) and 6(c) show the heat cycle characteristics of SiO_2 : $Eu(15C5)^{3+}Me_3SnSnMe_3$ and SiO_2 : $Eu(15C5)^{3+}$, respectively.

Figs. 7(a) and 7(b) are graphs showing heat cycle characteristics of optochemical hole burning media with SiO_2 : $Eu(15C5)^{3+}Me_3SiSiMe_3$ of other embodiment according to the present invention in which Fig. 7(a) shows the heat cycle characteristics of in the use of 3 mol% $Me_3SiSiMe_3$ for SiO_2 : $Eu(15C5)^{3+}Me_3SiSiMe_3$, and Figs. 7(b) the heat cycle characteristic in the use of 6% $Me_3SiSiMe_3$ for SiO_2 : $Eu(15C5)^{3+}Me_3SnSnMe_3$.

Figs. 8(a) to 8(d) are graphs showing excitation spectra of SiO_2 : M_xO_y (Si : M = 7 : 3) : $[Eu(15C5)]^{3+}$ (Eu^{3+} : 15C5 = 1 : 3) at 77K before and after laser irradiation.

Figs. 9(a) and 9(b) are graphs showing heat cycle characteristics of hole burning media of the SiO_2 : M_xO_y : $[Eu(15C5)]^{3+}$ media irradiated at 77K.

Figs. 10(a) and 10(b) are graphs showing heat cycle characteristics of hole burning media of SiO_2 : M_xO_y : $[Eu(15C5)]^{3+}$ at 77K.

Fig. 11 shows excitation spectra of SiO_2: $Eu(15C5)^{3+}$ C_9H_8 (indene) before and after irradiation with laser at 77 K and a differential spectrum therebetween.

Detailed Description of the Invention

[0020] The photochemical hole burning medium according to the present invention comprises a material in which a rare earth complex and a reducing agent dispersed in a solid matrix. That is, the present invention is directed to the optochemical hole burning medium using the material exhibiting the optochemical hole burning phenomenon.

[0021] In the present invention, the term "solid matrix" means host molecules of the optochemical hole burning medium, and is not particularly limited. For example, as the solid matrix, at least one glass-forming compound selected from the group consisting of silica, germanium oxide, boron oxide, phosphorus pentaoxide and tellurium oxide may be recited. Further, at least one compound selected from the group consisting of Al_2O_3, Ga_2O_3, In_2O_3, ZrO_2, Nb_2O_5 and Ta_2O_5 may be contained in the solid matrix. From the standpoint of easy productibity with use of a sol-gel method, silica may be recited as the solid matrix.

[0022] As the rare earth complex, at least one complex selected from the group consisting of a europium (III) crown ether complex, a europium (III) polyether complex, and a europium (III) cryptand complex may be recited.

[0023] In view of the fact that easy reduction from trivalent to a divalent state, which is considered to be a factor of inducing the optochemical hole burning effected, the europium (III) crown ether complex is preferred as the rare earth complex. As large ring compounds represented by the crown ether, large ring compounds having heteroatoms such as oxygen, nitrogen, sulfur, etc., e.g., 12-crown-4, 15-crown-5, 18-crown-6, 24-crown-8, dibenzo-18-crown-6, cryptand[2, 2], cryptand [2, 2, 2], etc. may be recited. In the present invention, such large ring compounds may be recited.

[0024] From the standpoint of easy complex formation of divalent europium ions, 15-crown-5 (hereinafter referred to as "15C5") is preferred as the crown ether.

[0025] The rare earth metals are not particularly limited, and Eu, Sm, Pr, etc. may be recited. From the easy complex formation of divalent europium ions, Eu may be recited as the rare earth element.

[0026] The reducing agent used in the present invention is not particularly limited so long as it can readily reduce the rare earth ions while not causing a reverse reaction and its absorption does not overlap with that of a zerophone line

of the rare earth ions. Preferably, organic molecular compounds which exhibit compatibility with the rare earth complex may be recited. From the standpoint of easy transportation of electrons with the rare earth ions, the reducing agent may be an electron-donating composite compound. As the electron-donating composite compound, a silane compound, a disilazane compound or the organic tin compound may be recited.

[0027] As the silane compound, at least one a hexaalkyl disilazane represented by hexamethyl disilane may be recited. As the disilazoneor, a hexaalkyldisilazane represented by hexamethyl disilazane may be recited. From the standpoint of being readily dissolved in a common solvent to be used in the sol-gel reaction, hexamethyl disilane and disilazane compound may be recited as the silane compound and the disilazane compound, respectively.

[0028] As the electron-donating composite compound, an organic tin compound may be used. As the organic tin compound, a compound represented by RSnSnR in which R is an alkyl group or an aryl group may be recited. From the standpoint of being readily dissolved in a common solvent to be used in the sol-gel reaction, R is preferably a methyl group.

[0029] The use amount of the reducing agent varies depending upon rare earth ions, complex ligands, solid matrixes, etc. as employed, and is not particularly limited. From the standpoint of maintaining the high hole stability, up to 20 mol% of the reducing agent may be used relative to the entire amount of the metal component constituting the solid matrix. The use amount is preferably 3 to 6 mol% from the standpoint of the transparency and light transmission of the medium.

[0030] According to a further preferable embodiment of the photochemical hole burning medium of the present invention, the reducing agent has an oxidation/reduction potential of not more than 1.5 V (vs. SCE). The reason is that the oxidation potential of E^{3+}/Eu^{2+} is about -0.43 V (vs. NHE), the Eu is converted to an excited state by irradiation with laser beam, and Eu^{3+} can be reduced to Eu^{+2}, if the oxidation/reduction potential is not more than 1.5 V (vs. SCE).

[0031] Therefore, any reducing organic molecule having the oxidation/reduction potential of not more than 1.5 V (vs. SCE) as the reducing agent can theoretically reduce Eu^{3+} to Eu^{2+} and can exhibit the hole burning effect.

[0032] Even other organic molecules having an oxidation/reduction potential of

more than 1.5 V (vs. SCE) can cause hole in relation to other rear earth complex. In such a case, the organic molecules having the oxidation/reduction potential of more than 1.5 V (vs. SCE) can be used.

[0033] Next, the method for producing the optochemical hole burning medium according to the present invention will be explained. The optochemical hole burning medium according to the present invention can be produced by using the ordinary sol-gel method, for example. The sol-gel method is generally a method in which a gel is obtained by dewatering a hydroxide-containing sol, and an inorganic oxide or the like having a given shape or in the form of a thin or thick film on a substrate is prepared by heating and drying the gel.

Examples

[0034] The present invention will be explained in more detail with reference to specific Examples, but the invention is never intended to be interpreted as being limited to these Examples.

Example 1

[0035] An optochemical hole burning medium using a solid matrix in which SiO_2 was added to ZrO_2 was prepared by the sol-gel method. The preparing procedure was as follows. A few or several drops of hydrochloric acid were added as a catalyst into a solution of $Si(OC_2H_5)_4 : H_2O : C_2H_5OH = 1 : 1 : 5$ (molar ratio), which was refluxed for one hour. Then, a metal alkoxide : $Zr(OC_2H_5)_4$ was added to the resulting solution such that $Si : Zr = 7 : 3, 5 : 5$ or $3 : 7$, followed by one hour refluxing. $EuCl_3 : H_2O : C_2H_5OH = 0.03 : 4 : 4 : 0.03$ was added to the resultant, which was subjected to drying at 50°C for 2 weeks or 90°C for 2 days. Thereby, $(SiO_2\text{-}ZrO_2) : [Eu(15C5)]^{3+}$ was obtained.

[0036] After the resulting sample was cooled by using a cryostat, a hole was formed through being irradiated with laser beam of rhodamine 6G colarant at 100 mW/mm^2 for 10 minutes. The stability of the hole was evaluated based on temperature cycles that the sample having a hole formed at 77K was heated to a given temperature, held at this temperature for about 1 minutes and cooled again to 77K.

[0037] More specifically, the hole was formed by irradiating laser beam at 77K upon each of samples in which 3 mol% of $EuCl_3$ and 9mol% of 15-crown-5(15C5) were incorporated into a ceramic material formed by mixing SiO_2 with ZrO_2 at a

given ratio.

[0038] Figs. 1(a), 1(b) and 1(c) show excitation spectra of ^7Fo-^5Do before and after the laser irradiation upon these samples.

[0039] As a result, it was seen that as the content of ZrO_2 in the solid matrix increased, the non-uniform width was enlarged. Thus, it is considered that the local structure near Eu^{3+} ions in the matrix became non-uniform due to the incorporation of ZrO_2. However, the depth of the hole formed decreased with increase in the incorporated amount of ZrO_2. Further, an anti-hole was seen in the case of $SiO_2 : ZrO_2 = 5 : 5$. This is interpreted such that the formation of a complex between Eu^{3+} ions and 15C5 was interrupted by the formation of a firm network.

[0040] Figs. 2(a), 2(b) and 2(c) show heat cycle characteristics of $(SiO_2\text{-}ZrO_2) : Eu(15C5)^{3+}$ each having a hole formed at 77K. Fig. 2(a) corresponds to $SiO_2 : ZrO_2 = 7 : 3$, Fig. 2(b) to $SiO_2 : ZrO_2 = 5 : 5$, and Fig. 2(c) to $SiO_2 : ZrO_2 = 3 : 7$.

[0041] When the ingredients constituting the matrix were $SiO_2 : ZrO_2 = 7 : 3$, the hole could be maintained up to 300K. When the ingredients constituting the matrix were $SiO_2 : ZrO_2 = 5 : 5$, the hole could be maintained up to 150K. When the ingredients constituting the matrix were $SiO_2 : ZrO_2 = 5 : 5$, the hole could be maintained up to 100K. This revealed that if the ZrO_2 is added at a high concentration, the hole-forming efficiency decreases and the hole cannot be maintained at high temperatures, although the non-uniform width increases.

Example 2

[0042] Next, in order to clarify a cause for the high hole-maintaining temperatures of the above-mentioned composite glasses, R6G laser beams at an intensity of 300 $mWmm^{-2}$ and a wavelength of 579.6 mm were irradiated upon $SiO_2 : Eu(15C5)^{3+}$ ($EuCl_3$ = 3 mol%, 15C5 = 9 mol%) at room temperature for 2 hours, and fluorescent spectra were examined before and after the irradiation. Results of the fluorescent spectra are shown in Figs. 3(a) and 3(b). As a result, it was clarified in the laser-irradiated samples that the intensity of light emission at 570 ~ 720 nm based on Eu^{+3} ions decreased, whereas fluorescent peak based on Eu^{+2} ions newly appeared at around 420 nm.

[0043] From the above, it was suggested that the optical reduction from Eu^{3+} ions to Eu^{2+} ions was caused as the PSHB mechanism by the laser irradiation.

Example 3

[0044] From the results stated in Example 2, it was clarified that the reduction from Eu^{3+} to Eu^{2+} can exhibit excellent hole-maintaining characteristic.

[0045] Thus, various reducing agents were dispersed in trial into solid matrixes together with rare earth complexes.

[0046] First, tests were performed with a silane compound being used as a reducing agent. More specifically, SiO_2 : $Eu(15C5)^{3+}$, $Me_3SiSiMe_3$ was prepared. The preparing procedure was as follows. A few or several drops of hydrochloric acid were added as a catalyst into a solution of $Si(OC_2H_5)_4$: H_2O : C_2H_5OH = 1 : 1 : 5 (molar ratio), which was refluxed for one hour. Then, $EuCl_3$: H_2O : C_2H_5OH : 15C5 : $Me_3SiSiMe_3$ = 0.03 : 4 : 4 : 0.03 : 0.06 (molar ratio) were added to the resulting solution, which was subjected to drying at 50°C for one week or at 90°C for 2 days. Thereby, SiO_2 : $Eu(15C5)^{3+}$, $Me_3SiSiMe_3$ was obtained. Loaded compositions for typical glass materials are shown in Table 1.

[0047]

Table 1

Loaded composition for the typical glass materials

TEOS (1:1:5) reflux liquid :	$EuCl_3$:	H_2O :	C_2H_5OH :	15-crown-5 :	$Me_3SiSiMe_3$ (molar ratio)
1	0.03	4	4	0.03	0.06
1	0.03	4	4	0	0.06
TEOS (1:1:5) reflux liquid :	$EuCl_3$:	H_2O :	C_2H_5OH :	15-crown-5 :	$Me_3SiSiMe_3$
1	0.03	4	4	0.03	0.03
1	0.03	4	4	0	0.03

[0048] Samples to which neither $Me_3SiSiMe_3$ nor the crown ether was added were prepared in the same manner.

[0049] In the same manner as mentioned above, SiO_2 : $Eu(15C5)^{3+}$, $Me_3SnSnMe_3$ was obtained.

[0050] With respect to the hole burning characteristic, a holes was formed by using rhodamine 6G colarant laser. Heat cycle tests were effected such that after the hole was formed at 77K, then the temperature was successively raised to 100K, 150K, 200K, 250K and 300 K, the temperature of 300K was maintained for about 1 minute and returned to 77K again, and an excitation spectrum was measured.

[0051] Figs. 4(a) and 4(b) show excitation spectra and differential spectra of SiO_2 : $Eu(15C5)^{3+}$, $Me_3SiSiMe_3$ and SiO_2 : $Eu(15C5)^{3+}$, $Me_3SnSnMe_3$ before and after the laser irradiation at 77K, respectively.

[0052] An excitation spectrum corresponding to ^7Fo-5Do transition of Eu^{3+} ions in a wavelength range of 579 to 581 nm was observed in the samples not irradiated. When the rhodamine 6G colarant laser was irradiated upon these samples at a rate of 100 mW/mm^2 for 600 seconds, a half-value width of 0.125 nm was observed as shown in Figs. 4(a) and 4(b).

[0053] In the sample with no crown ether added, no hole was formed, although the intensity of the light emission over the entire spectrum merely decreased through being irradiated with the laser. This revealed that as compared with the Eu^{3+} ions alone, the Eu^{3+} ions forming a complex with the crown ether more readily receive electrons from in the matrix $Me_3SiSiMe_3$ when in the erected state, so that they can more effectively form the hole.

[0054] Spectra were observed with respect to SiO_2 : $Eu(15C5)^{3+}$ and $Me_3SnSnMe_3$. Fig. 5 shows an excitation epectrum and a differential spectrum of SiO_2 : $Eu(15C5)^{3+}$, Me_3SnSMe_3 at 77K before and after the laser irradiation.

[0055] As a result, the formation of hole was confirmed with respect to $Me_3SnSnMe_3$ to which the crown ether was incorporated (half-value width 0.141 nm). With respect to the sample containing no crown ether, no hole was formed. Therefore, it was clarified that as compared with the Eu^{3+} ions alone, the Eu^{3+} ions forming a complex with the crown ether more readily receive electrons from $Me_3SnSnMe_3$ in the matrix when in the erected state, so that they can more effectively form the holes.

Example 4

[0056] Next, the heat cycle characteristic was examined with respect to an optochemical hole burning medium according to one embodiment of the present invention.

[0057] First, SiO_2 : $Eu(15C5)^{3+}Me_3SiSiMe_3$, SiO_2 : $Eu(15C5)^{3+}Me_3SnSnMe_3$ and SiO_2 : $Eu(15C5)^{3+}$ were prepared. SiO_2 : $Eu(15C5)^{3+}Me_3SnSnMe_3$ was prepared in the same manner as in Example 3 except that $Me_3SnSnMe_3$ was used instead of $Me_3SiSiMe_3$. Further, SiO_2 : $Eu(15C5)^{3+}$ was prepared in the same manner as in Example 3 except that no electron-donating composite compound was used.

[0058] With respect to these samples, the heat cycle characteristic was examined. That is, the heat cycle characteristic of a hole formed at 77K in each of the SiO_2, $Eu(15C5)^{3+}Me_3SiSiMe_3$ and SiO_2 : $Eu(15C5)^{3+}Me_3SnSnMe_3$ in a temperature range of 77 to 300K were examined. Results are shown in Figs. 6(a) to 6(c). Fig. 6(a) shows a heat cycle characteristic of SiO_2 : $Eu(15C5)^{3+}Me_3SiSiMe_3$, and Figs. 6(b) and 6(c) shows heat cycle characteristics of SiO_2 : $Eu(15C5)^{3+}Me_3SnSnMe_3$ and SiO_2 : $Eu(15C5)^3$, respectively.

[0059] In the SiO_2 : $Eu(15C5)^{3+}Me_3SiSiMe_3$, the hole was maintained up to 300K. In the SiO_2 : $Eu(15C5)^{3+}Me_3SnSnMe_3$, the hole was maintained up to 250K.

[0060] With increase in temperature, the uniform width increases, whereas the depth of the holes decreases. When the sample contains $Me_3SiSiMe_3$, the holes having about 70% of that of the holes at 77K with the half-value width of 0.479 nm was maintained at 300K. When the sample contains $Me_3SnSnMe_3$, the hole having about 61% of that of the hole at 77K with the half-value width of 0.474 nm was maintained at 250K.. Therefore, it is seen that the medium to which the reducing agent is added has improved temperature stability of the hole as compared with the crown ether complex alone. This is considered such that when Me_3MMMe_3 (M = Si or Sn) functioning as the reducing agent is incorporated, the M-M bond is cleaved through the reduction to make a reverse reaction difficult to occur.

Example 5

[0061] Next, the heat cycle characteristic was examined while the concentration of the reducing agent was varied. Samples were prepared according to the method described in Example 3. $Me_3SiSiMe_3$ was used as the reducing agent.

[0062] Results on the heat cycle characteristic are shown in Figs. 7(a) and 7(b). Figs. 7(a) and 7(b) show the heat cycle characteristics of SiO_2 : $Eu(15C5)^{3+}Me_3SiSiMe_3$ in which Figs. 7(a) and 7(b) correspond to uses of 3 mol% and 6 mol% of $Me_3SiSiMe_3$, respectively.

[0063] As obvious from Figs. 7(a) and 7(b), it is seen that the case using 6 mol% of $Me_3SiSiMe_3$ exhibited higher stability of the hole as compared with the case using 3 mol% of $Me_3SiSiMe_3$. This is considered such that increase in $Me_3SiSiMe_3$ increased the amount of $Eu(15C5)^{3+}$, so that the holes became difficult to return correspondingly.

Example 6

[0064] Next, spectra were examined when the solid matrix was modified. Solid matrixes in which Al_2O_3, TiO_2 or Ta_2O_5 was incorporated into SiO_2 were used. Samples were prepared similarly according to the method described in Example 1.

[0065] Laser were irradiated upon each of these samples, and their excitation spectra were observed. Figs. 8(a) to 8(d) show excitation spectra of SiO_2-MxOy (Si : M = 7 : 3) : $[Eu(15C5)^{3+}]^{3+}$ (Eu^{3+} : 15C5 = 1 : 3) at 77K before and after laser irradiation.

[0066] In each of the cases, the depth of the hole was not conspicuously different from that in the case with SiO_2 alone.

[0067] With respect to the width of the hole, when Al_2O_3 was introduced into SiO_2, Al^{3+} bonds to non-crosslinking oxygen to form a network as [AlO_4]. Thereby, the local structure near the Eu^{3+} ions is strengthened to narrow the width of the hole. It is considered that similar effect is produced in the case of the incorporation of ZrO_2 and Ta_2O_5.

[0068] To the contrary, when TiO_2 was incorporated into SiO_2, the hole width tended to increase as compared with SiO_2. This is considered that [TiO_4] bonds to the crosslinking oxygen rather than non-crosslinking oxygen.

[0069] Next, the heat cycle characteristic of the above samples was examined. Figs. 9 and 10 show the heat cycle characteristics of holes formed at 77K in SiO_2-MxOy : $[Eu(15C5)]^{3+}$.

[0070] In each case, the hole was confirmed after the heat cycles down to room temperature. Particularly, the incorporation of ZrO_2 and Ta_2O_5 retained deeper holes at room temperature as compared with Al_2O_3.

[0071] Any of the solid matrixes used exhibited high stability of the holes at high temperatures. This is considered such that the local structure near the Eu^{3+} ions was strengthened and the lattice vibration was suppressed by the addition of the heavy element.

[0072] The hole burning medium according to the present invention has the advantageous effect that signals can be written therein depending upon the wavelength of the laser beam irradiated.

Example 7

[0073] A photochemical hole burning medium was prepared in the same manner

as in Example 1, and tested in the same manner as in Example 3 except that indene was used as a reducing agent.

[0074] Fig. 11 shows excited spectra of SiO_2: $Eu(15C5)^{3+}$, indene before and after irradiation with laser at 77 K and a differential spectrum therebetween.

[0075] As a result, formation of a hole was confirmed. From this result, it is seen that any reducing agent can well function as the reducing agent and form a stable hole, so long as its oxidation/reduction potential is equal to or lower than that of indene. The oxidation/reduction potentials of organic molecules are summarized in below Table 2.

[0076]

Table 2

reducing agents	$E^0(D^+/D)$
N, N, N, N-tetramethyl-p-phenylene diamine	0.16
N, N, N, N-tetramethyl benzidine	0.32
1, 4-diazabicyclo[2, 2, 2]octane	0.57
hexamethyl ditin	0.68
N, N-dimethylaniline	0.76
hexamethyl disilane	0.92
triethylamine	0.96
2-methoxynaphthalene	1.42
1, 1-diphenylethylene	1.52
indene	1.52

[0077] It is seen that the reducing agents shown in Table 2 all have the oxidation/reduction potentials lower than that of indene, and are well used.

[0078] The hole burning medium according to the present invention has the advantageous effect that it enables the wavelength-multiple type optical memory operable at room temperature.